

CRYSTALLINE STRUCTURES AND COMPOSITIONAL DEPTH PROFILE OF
SOLUTION DERIVED LEAD-FREE $(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ (BNBT) THIN FILMS AROUND
THE MORPHOTROPIC PHASE BOUNDARY

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$(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ (BNBT) is considered a promising lead-free alternative to MPB- $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT). It shows the coexistence of rhombohedral (R3c) and tetragonal (P4mm) crystalline structures in the proximity to the MPB ($x \sim 0.06$). In this work, BNBT thin films were fabricated by chemical solution deposition (CSD) with a wide range of compositions ($x=0.050$ - 0.150) onto $\text{Pt}/\text{TiO}_2/\text{SiO}_2/(100)\text{Si}$ substrates, from hybrid precursor solutions. Stoichiometric thin films (hereinafter BNBT) and others containing $\text{Na}^+\text{Bi}^{3+}$ excesses (BNBTxs) were prepared. Na^+ and Bi^{3+} are highly volatile at the crystallization temperatures, and traditionally small excesses of these elements are added to the precursor solution to compensate any possible loss. Structural studies by X-ray diffraction using the $\lambda_{\text{Cu}}=1.54 \text{ \AA}$ and synchrotron radiation with $\lambda=0.97354 \text{ \AA}$ were performed to determine the crystalline structure of the films. Rietveld analysis of the experimental X-ray patterns showed different phase volume fractions of the rhombohedral-tetragonal phases as a function of the Ba^{2+} content and a shift of the position of the MPB with the introduction of $\text{Na}^+\text{Bi}^{3+}$ excesses. MPB was around $x \sim 0.055$ and $x \sim 0.10$ for the BNBT and BNBTxs, respectively. Rutherford backscattering experiments (RBS) were performed to study the compositional profile of the films. This study revealed bismuth excess is not volatilized during crystallization of the BNBTxs films, but forming instead thick Bi_xPt bottom interfaces. RBS also indicated that the BNBT films with $x \sim 0.055$ have a homogeneous compositional profile and again it is confirmed the coexistence of rhombohedral and tetragonal phases, which is accompanied by well-defined ferroelectric hysteresis loops with comparatively high values of remnant polarizations.

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